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# ADSORPTION OF DIRECT DYE ON CELLULOSE IN THE PRESENCE OF SODIUM ALGINATE AT VARIOUS TEMPERATURES

M. Nango, S. Tanihara, M. Maekawa, A. Katayama† and N. Kuroki

*Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka, Japan*

## SUMMARY

*Dyeing of cellulose by Chrysophenine G (CI Direct Yellow 12) in aqueous sodium alginate solution at various temperatures has been studied. The effect of temperature change on dye adsorption equilibrium to cellulose in the presence of sodium alginate has been examined based on the previously described multiple equilibrium model. The affinities of the dye, which were calculated with an interpolated ionisation degree of the carboxyl group in the cellulose and by using the ionization degree of sodium alginate measured were nearly constant under the present dyeing conditions. These results confirm the previous conclusion that the dye is concentrated into the internal solution of cellulose due to the presence of sodium alginate in the bulk solution.*

## 1. INTRODUCTION

In previous papers,[1,2] the adsorption of direct dye on cotton in the presence of sodium alginate(polyelectrolyte) at 90°C has been described. The application of the membrane equilibrium theory suggested that the dye was concentrated in the internal solution of cellulose by the presence of sodium alginate in the bulk solution. However, it was difficult to consider the role of sodium alginate clearly because of its hydrolysis during the course of dyeing. In this report, dyeing of cotton and cellophane by Chrysophenine G in aqueous sodium alginate solution at various temperatures has been studied. The effect of

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† Present address: Kyoto Women's University, Kyoto, Japan

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temperature change on the dye adsorption equilibrium in the presence of sodium alginate and on the degree of ionisation of sodium alginate in aqueous solution has been examined based on the previously described model for this dyeing system. The affinities of the dye, which were calculated using the measured degree of ionisation of the carboxyl groups in the cellulose gave nearly constant values under the present dyeing conditions.

## 2. MATERIALS AND METHODS

### 2.1. *Materials*

Chrysophenine G (CI Direct Yellow 12, Fig. 1) obtained from Sumitomo Chemical Ind. Co. was purified by the method of Robinson and Mills.[3] Analar sodium chloride was added to the dye solutions. Sodium alginate (Fig. 2) supplied by Tokai Senko Co. was purified by the method as described in the previous papers.[1,2] The molecular weight determined by the viscosity method (1N NaCl at 25°C)[1,4] was $10^5$. The molecular weight decreased from $10^5$ to $5 \times 10^4$ by hydrolysis during the course of dyeing at 90°C.[1] The average dimension of sodium alginate (MW $5 \times 10^4$) was calculated as $127 \times 10^{-8}$ cm.[1] The degree of ionisation, $\alpha$, in aqueous sodium alginate solutions with and without added sodium chloride was determined by the method of Okubo *et al.*[5] at 25° and 50°C using sodium glass electrodes (Horiba Manufacturing Co., Kyoto), calibrated with the standard solution of sodium chloride. The value of $\alpha$ was $0{\cdot}5 \pm 0{\cdot}05$ with the concentration of electrolytes used. The change of $\alpha$ with the hydrolysis of sodium alginate caused during the course of dyeing and with temperature change from 25° to 50°C was not observed.[1,2] The pH value in the solution after dyeing was 6·5 under conditions with and without sodium alginate. The binding of dye to sodium alginate was negligible as determined by the dialysis equilibrium method.[6] The concentration of sodium alginate is given in pyranose unit mole (see Fig. 2). Deionised and distilled water was used to prepare the solutions. Cotton and cellophane were purified as described in the previous papers.[1,7] Carboxyl group contents of cotton and cellophane determined by iodometry[8] were 4·00 and 62·5 meq kg$^{-1}$, respectively.

### 2.2. *Dyeing procedure*

Dyeing was carried out as described in the previous papers.[1,2] The dyeings of cotton and cellophane were made at 50°C and 70°C, respectively, for 6 h.

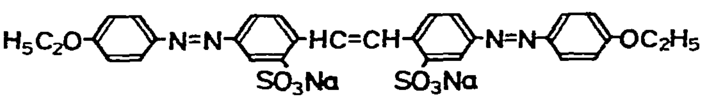

Fig. 1. Chrysophenine G (CI Direct Yellow 12). The basicity of dye anion ($z$) = 2.

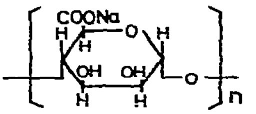

Fig. 2. Sodium alginate (NaAlg). *n*: pyranose unit molar structure; ionisation degree ($\alpha$): 0·5 at 25° and 50°C.

### 2.3. *Solution of equation*

Calculations were performed by using a Nonc. 50 with Fortran programs.

## 3. RESULTS AND DISCUSSION

Figure 3 shows the adsorption of dye at various temperatures in the system with sodium alginate successively added. The adsorption curves at various concentrations of sodium alginate used show the increasing dye adsorption with increasing sodium alginate addition at two temperatures studied as well as at 90°C as described previously.[1,2] Figures 4 and 5 show the adsorption isotherms of dye on cotton and cellophane respectively at various temperatures in aqueous solutions of 0·02 unit molar sodium alginate and of 0·01 molar sodium chloride, in which the concentration of sodium ion is almost the same in the bulk solution for both electrolytes used because the degree of ionization of sodium alginate is almost half that of sodium chloride. The adsorption isotherms of the dye on cotton in aqueous sodium alginate solutions at 70° and

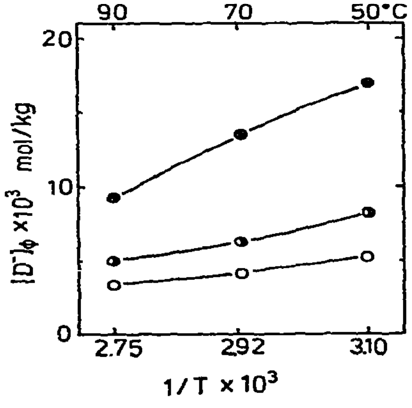

Fig. 3. The adsorption of Chrysophenine G on cotton in the system containing sodium alginate (NaAlg) successively added at 50°, 70° and 90°C. Concentration of NaAlg (pyranose unit mol): ○, 0·02 mol dm$^{-3}$; ◑, 0·04 mol dm$^{-3}$; ●, 0·01 mol dm$^{-3}$. Concentration of dye: $2 \times 10^{-3}$ mol dm$^{-3}$. Data at 90°C are cited from ref. 1.

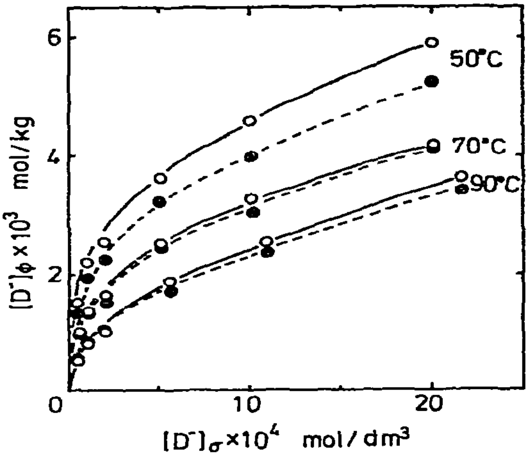

Fig. 4. Adsorption isotherms of Chrysophenine G on cotton in aqueous solutions of sodium alginate (NaAlg) and of sodium chloride at various temperatures. ●: 0·02 pyranose unit molar NaAlg; ○: 0·10 molar sodium chloride; Data at 90°C are cited from ref. 1.

90°C in Fig. 4 are similar to those in aqueous sodium chloride solution. However, the adsorption isotherms of dye on cotton at 50°C and on cellophane at all temperatures in aqueous sodium alginate solution differ significantly from those in aqueous sodium chloride solution. The average dimension of sodium alginate ($127 \times 10^{-8}$ cm: MW $5 \times 10^4$)[1] is too large to enter the pore of cellulose ($40 \times 10^{-8}$ cm) so that its role in the dyeing of cellulose must differ from that of an inorganic electrolyte like sodium chloride which is small.

For the quantitative interpretation of the role of sodium alginate in the bulk solution on equilibrium adsorption of dye, the following theoretical treatment was applied to the present results as described in the previous paper.[2] As envisaged in the adsorption model on cellulose in Fig. 6, dye is assumed to be adsorbed in the internal solution of cellulose ($i$ phase). Bulk phase ($\sigma$) is assumed to penetrate into the pores of cellulose and this portion of it is designated as $\gamma$. It is assumed that the sodium alginate ion ($P_n^-$) is present only in the $\sigma$ phase.

According to Donnan membrane equilibrium between the two phases, the ionic concentrations are related as follows;

$$[\mathrm{Na}^+]_\sigma^z[\mathrm{D}^-]_\sigma = [\mathrm{Na}^+]_\gamma^z[\mathrm{D}^-]_\gamma = [\mathrm{Na}^+]_i^z[\mathrm{D}^-]_i \tag{1}$$

$$[\mathrm{Na}^+]_\sigma[\mathrm{Cl}^-]_\sigma = [\mathrm{Na}^+]_\gamma[\mathrm{Cl}^-]_\gamma = [\mathrm{Na}^+]_i[\mathrm{Cl}^-]_i \tag{2}$$

where $z$ is the basicity of the dye anion ($z = 2$).

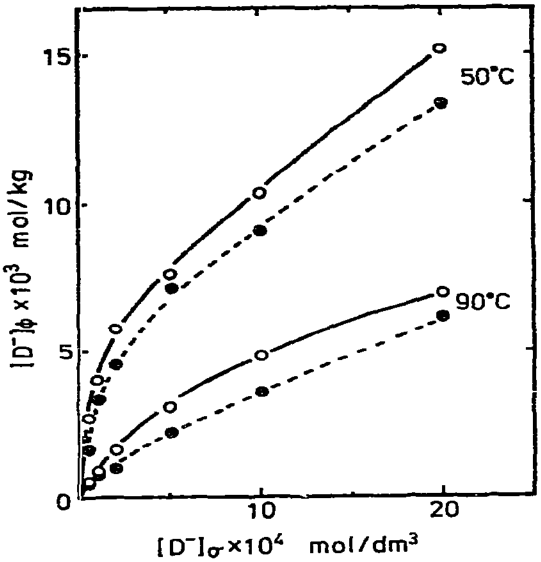

Fig. 5. Adsorption isotherms of Chrysophenine G on cellophane in aqueous solutions of sodium alginate (NaAlg) and of sodium chloride at 50° and 90°C. ●: 0·02 pyranose unit molar NaAlg; ○: 0·01 molar sodium chloride.

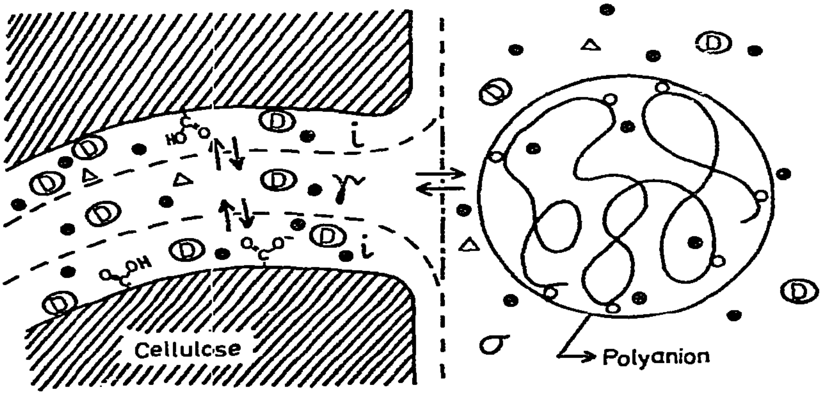

Fig. 6. Adsorption model on cellulose. Sodium alginate ion (polyanion, $P_n^-$) is present only in the bulk (σ) phase. Ⓓ, dye anion; ●, sodium ion; △, chloride ion. ○, $P^-$, alginate anion shown with pyranose unit mol; *i*, internal solution of cellulose; σ, bulk phase; γ, bulk phase assumed to penetrate into the pores of cellulose.

For maintaining electrical neutrality in each phase,

$$\sigma \text{ phase: } [\mathrm{Na}^+]_\sigma = z[\mathrm{D}^-]_\sigma + \alpha[\mathrm{P}^-]_\sigma + [\mathrm{Cl}^-]_\sigma \tag{3}$$

where $\alpha[\mathrm{P}^-]_\sigma$ represents the concentration of alginate ion shown with pyranose unit mole (see Fig. 2) and $\alpha$ represents the measured degree of ionisation of sodium alginate ($\alpha = 0{\cdot}50$).

$$\gamma \text{ phase: } [\mathrm{Na}^+]_\gamma = z[\mathrm{D}^-]_\gamma + [\mathrm{Cl}^-]_\gamma \tag{4}$$

$$i \text{ phase: } [\mathrm{Na}^+]_i = \frac{z[\mathrm{D}^-]_\phi}{V} + [\mathrm{Cl}^-]_i + \frac{\beta[\mathrm{COOH}]_\phi}{V} \tag{5}$$

where $V$ represents the volume term of $i$ phase (cotton: 0·22 dm$^3$ kg$^{-1}$, cellophane: 0·33 dm$^3$ kg$^{-1}$),[9] $[\mathrm{COOH}]_\phi$ represents the carboxyl group content (cotton: 4 meq kg$^{-1}$, cellophane: 62·5 meq kg$^{-1}$), $\beta$ is the ionisation degree of carboxyl group in the cellulose, and $[\mathrm{D}^-]_\phi$ is the concentration of dye ion adsorbed on cellulose in mol kg$^{-1}$ dry fibre.

Combining eqns (2) and (4), $[\mathrm{Na}^+]_i$ is obtained, where $[\mathrm{Na}^+]_\phi = V[\mathrm{Na}^+]_i$ and $[\mathrm{Na}^+]_\phi$ is the concentration of sodium ion adsorbed in the cellulose in mol kg$^{-1}$ dry fibre.

The following equation was used to calculate the standard free energy of dyeing ($\Delta\,\mu^0$).[9]

$$-\Delta\,\mu^0 = RT \ln [\mathrm{Na}^+]_\phi^z[\mathrm{D}^-]_\phi / V^{z+1}[\mathrm{Na}^+]_\gamma^z[\mathrm{D}^-]_\gamma \tag{6}$$

$$= RT \ln [\mathrm{Na}^+]_\phi^z[\mathrm{D}^-]_\phi / V^{z+1}[\mathrm{Na}^+]_\sigma^z[\mathrm{D}^-]_\sigma \tag{7}$$

The calculated results, which were obtained by assuming $\beta = 0{\cdot}10$ as in the previous paper,[7] are given in Tables 1–3. Table 1 shows the affinity values and equilibrium adsorptions of dye on cotton and cellophane in aqueous sodium alginate solutions containing the constant concentration of sodium chloride at

TABLE 1

AFFINITIES AND EQUILIBRIUM ADSORPTIONS OF CHRYSOPHENINE G ON COTTON AND CELLOPHANE IN AQUEOUS SODIUM ALGINATE (NaAlg) SOLUTIONS CONTAINING A CONSTANT CONCENTRATION OF SODIUM CHLORIDE AT 50°C.

| *Cellulose* | NaAlg $\times 10^2$ mol dm$^{-3}$ | $[\mathrm{Na}^+]_\sigma \times 10^2$ mol dm$^{-3}$ | $[\mathrm{D}^-]_i \times 10^5$ mol dm$^{-3}$ | $[\mathrm{Na}^+]_i \times 10^2$ mol dm$^{-3}$ | $[\mathrm{D}^-]_\phi \times 10^4$ mol kg$^{-3}$ | $-\Delta\mu^0$ KJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| *Cotton* | 2·00 | 2·02 | 3·02 | 3·68 | 34·4 | 16·8 |
| | 4·00 | 3·02 | 3·64 | 5·01 | 48·4 | 17·2 |
| | 10·00 | 6·02 | 7·43 | 6·98 | 67·3 | 16·2 |
| *Cellophane* | 2·00 | 2·02 | 1·09 | 6·11 | 64·2 | 20·1 |
| | 4·00 | 3·02 | 1·54 | 7·68 | 89·0 | 20·0 |
| | 10·00 | 6·02 | 2·47 | 12·11 | 160·4 | 20·4 |

NaCl: $1{\cdot}00 \times 10^{-2}$ mol dm$^{-3}$. $[\mathrm{D}^-]\sigma$: $1{\cdot}00 \times 10^{-4}$ mol/dm$^3$

TABLE 2

AFFINITIES AND EQUILIBRIUM ADSORPTIONS OF CHRYSOPHENINE G ON COTTON IN AQUEOUS SODIUM ALGINATE (NaAlg) SOLUTIONS CONTAINING A CONSTANT CONCENTRATION OF SODIUM CHLORIDE AT 70°C.

| NaAlg $\times 10^2$ mol dm$^{-3}$ | $[Na^+]_\sigma$ $\times 10^2$ mol dm$^{-3}$ | $[D^-]_i$ $\times 10^5$ mol dm$^{-3}$ | $[Na^+]_\phi$ $\times 10^2$ mol dm$^{-3}$ | $[D^-]_i$ $\times 10^4$ mol kg$^{-1}$ | $-\Delta\mu°$ KJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 2·00 | 2·02 | 5·30 | 2·77 | 22·5 | 15·0 |
| 4·00 | 3·02 | 7·34 | 3·52 | 29·3 | 14·8 |
| 10·00 | 6·02 | 12·39 | 5·41 | 47·3 | 14·7 |

NaCl: $1{\cdot}00 \times 10^{-2}$ mol dm$^{-3}$, $[D^-]_\sigma$: $1{\cdot}00 \times 10^{-4}$ mol dm$^{-3}$

50°C and Table 2 shows those of dye on cotton at 70°C. The affinity values of dye on cotton and cellophane at 50°C and those of dye on cotton at 70°C are almost constant for the concentration change of sodium alginate as well as those of dye at 90°C in the previous paper.[2] These results shown in Tables 1 and 2 compare with those for various dye concentrations (Table 3). Thus, Table 3 shows that the affinity values of dye on cotton and cellophane at 50°C are almost constant for the concentration change of dye, too.

The affinity values which are nearly constant with various changes in the experimental conditions at 50° and 70°C confirm the correct assumption of the degree of ionisation of sodium alginate at 90°C in the previous papers[1,2] and of the interpolated degree of ionisation of the carboxyl group in the cellulose. Johnson *et al.*,[10] McGregor[11] and ourselves[7] have reported that the calculated affinities of some other direct dyes on cellulose are constant, using 0·1–0·25 for the ionization degree of the carboxyl group in the cellulose. The constant

TABLE 3

AFFINITIES AND EQUILIBRIUM ADSORPTIONS OF CHRYSOPHENINE G ON COTTON AND CELLOPHANE IN AQUEOUS SODIUM ALGINATE (NaAlg) SOLUTIONS CONTAINING SODIUM CHLORIDE AT 50°C.

| *Cellulose* | $[D^-]_\sigma$ $\times 10^4$ mol dm$^{-3}$ | $[Na^+]_\sigma$ $\times 10^2$ mol dm$^{-3}$ | $[D^-]_i$ $\times 10^5$ mol dm$^{-3}$ | $[Na^+]_i$ $\times 10^2$ mol dm$^{-3}$ | $[D^-]_\phi$ $\times 10^4$ mol kg$^{-1}$ | $-\Delta\mu°$ KJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| *Cotton* | 0·50 | 2·01 | 2·20 | 3·03 | 26·1 | 16·9 |
| | 1·00 | 2·02 | 3·02 | 3·68 | 34·4 | 16·8 |
| | 2·00 | 2·04 | 4·35 | 4·37 | 43·0 | 16·4 |
| | 5·00 | 2·10 | 7·48 | 5·43 | 55·4 | 15·6 |
| | 10·00 | 2·20 | 10·67 | 6·74 | 70·5 | 15·3 |
| *Cellophane* | 0·50 | 2·01 | 0·88 | 4·78 | 40·8 | 19·4 |
| | 1·00 | 2·02 | 1·09 | 6·11 | 64·2 | 20·1 |
| | 2·00 | 2·04 | 1·67 | 7·07 | 80·7 | 19·6 |
| | 5·00 | 2·10 | 2·34 | 9·69 | 125·0 | 19·8 |
| | 10·00 | 2·20 | 3·35 | 12·02 | 164·0 | 19·6 |

NaCl: $1{\cdot}00 \times 10^{-2}$ mol dm$^{-3}$, NaAlg: $2{\cdot}00 \times 10^{-2}$ mol dm$^{-3}$

affinities listed in Tables 1–3, which were found at various temperatures and on different kinds of celluloses, may be taken as indicating the basic soundness of our assumption proposed so far.[1,2,7,12,13]

It is interesting that the dye concentration in material phase, $[D^-]_i$, shown in Table 1 and Table 2, respectively, apparently increases with the addition of sodium alginate. The dye is concentrated into the internal solution of cellulose due to the presence of sodium alginate in the bulk solution.

These and previous results[1,2] lead to the conclusion that dyeing of cellulose by a direct dye in aqueous sodium alginate solution is quite reasonably explained on the model proposed.

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